

# Impact of Sulfur Oxides on Mercury Capture by Activated Carbons

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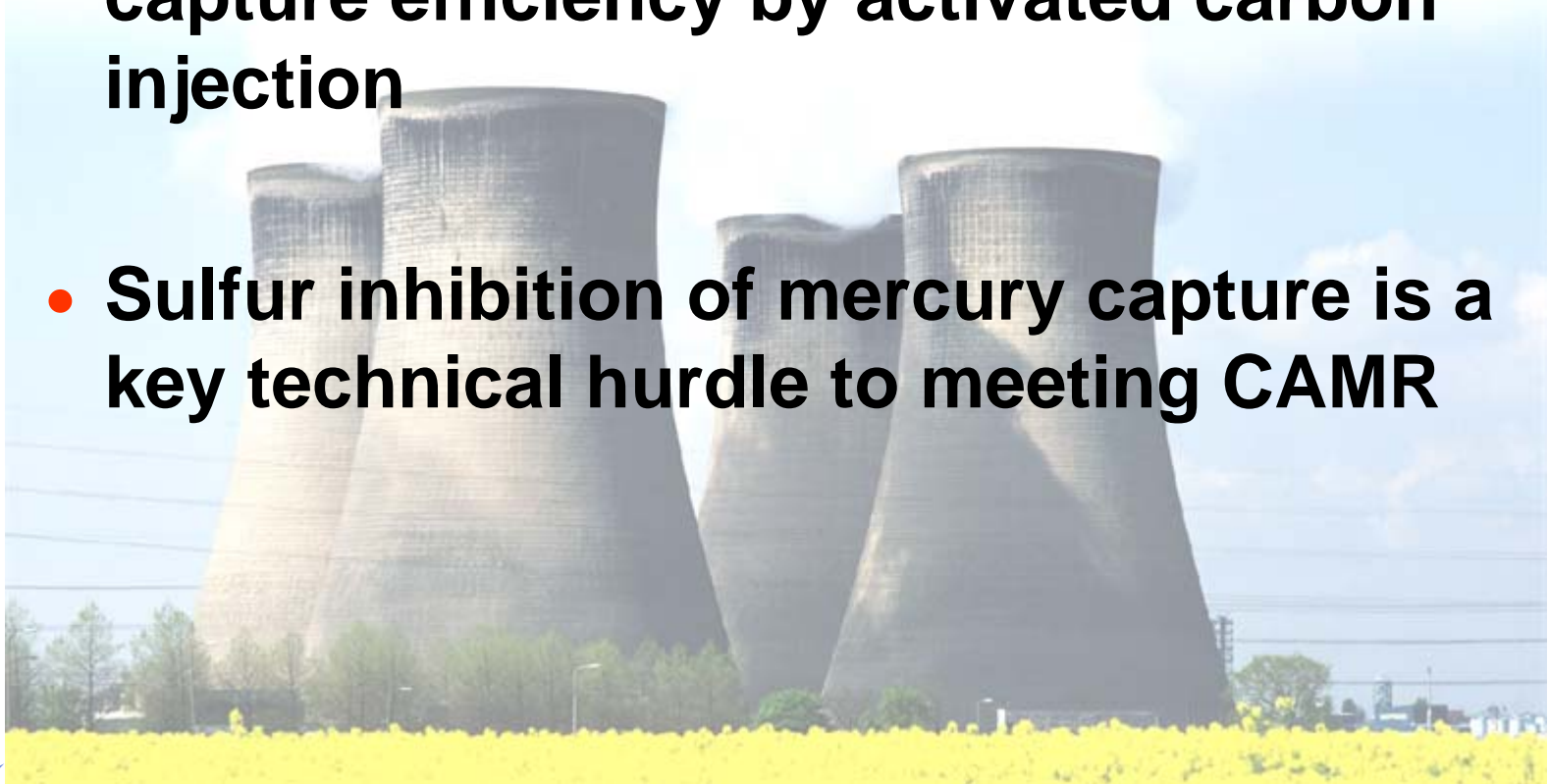
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# Challenge

- **Power plants with high concentrations of sulfur oxides show decreased mercury capture efficiency by activated carbon injection**
- **Sulfur inhibition of mercury capture is a key technical hurdle to meeting CAMR**



# Sulfur Oxides (SO<sub>x</sub>) in Flue Gas

- **Coal - S oxidized in the furnace primarily to sulfur dioxide (SO<sub>2</sub>), with small amounts of sulfur trioxide (SO<sub>3</sub>)**
  - SO<sub>2</sub> concentrations range from hundreds of ppm to over 1,000 ppm and SO<sub>3</sub> concentrations are generally 0 – 30 ppm
- **SO<sub>3</sub> (ppm levels) is injected into the flue gas as a conditioning agent to improve ESP performance**
- **SO<sub>3</sub> can form from the oxidation of SO<sub>2</sub> across SCR catalysts**

# High - SO<sub>x</sub> Mercury Capture Examples

- **AEP Conesville**

- High-sulfur coal, ~ 30 ppm SO<sub>3</sub> in flue gas
- Maximum mercury capture: 31% (Darco E-12 at 12 lb/MMacf)

- **Mississippi Power Plant Daniel**

- 6 ppm SO<sub>3</sub> reduced native mercury capture by 40% and effectiveness of ACI (Darco Hg at 10 lb / MMacf) by 25 – 35%

- **Other utilities see same inhibiting effect of SO<sub>3</sub>**

- **Laboratory results at EERC**

- Adding 1600 ppm SO<sub>2</sub> to simulated flue gas (with NO<sub>2</sub> present) caused previously captured Hg<sup>2+</sup> to desorb from carbon



# Possible Mechanisms for SO<sub>x</sub> Effect

- **Competitive adsorption between Hg and SO<sub>x</sub>**
  - SO<sub>2</sub> and SO<sub>3</sub> compete with Hg for Lewis base sites on the carbon surface
  - SO<sub>x</sub> capture could be favored kinetically & thermodynamically
    - SO<sub>2</sub> has a strong binding energy (~ 80 kJ mol<sup>-1</sup>) to activated carbon
    - Concentrations of SO<sub>2</sub> (100s – >1000 ppm) and SO<sub>3</sub> (0 – 10s ppm) are much greater than the concentration of Hg (~1 ppb)
  - Activated carbon catalyzes formation of S(VI)
    - $\text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{SO}_4$ 
      - Oxygen source can either be flue gas (O<sub>2(g)</sub>) or surface-bound oxygen
    - Activated carbon is a catalyst to oxidize SO<sub>2</sub>
    - H<sub>2</sub>SO<sub>4</sub> has low volatility (P<sub>VAP</sub> = 1 torr at 300° F)
    - NO<sub>2</sub> or another electron sink may be required to have a high conversion to sulfate

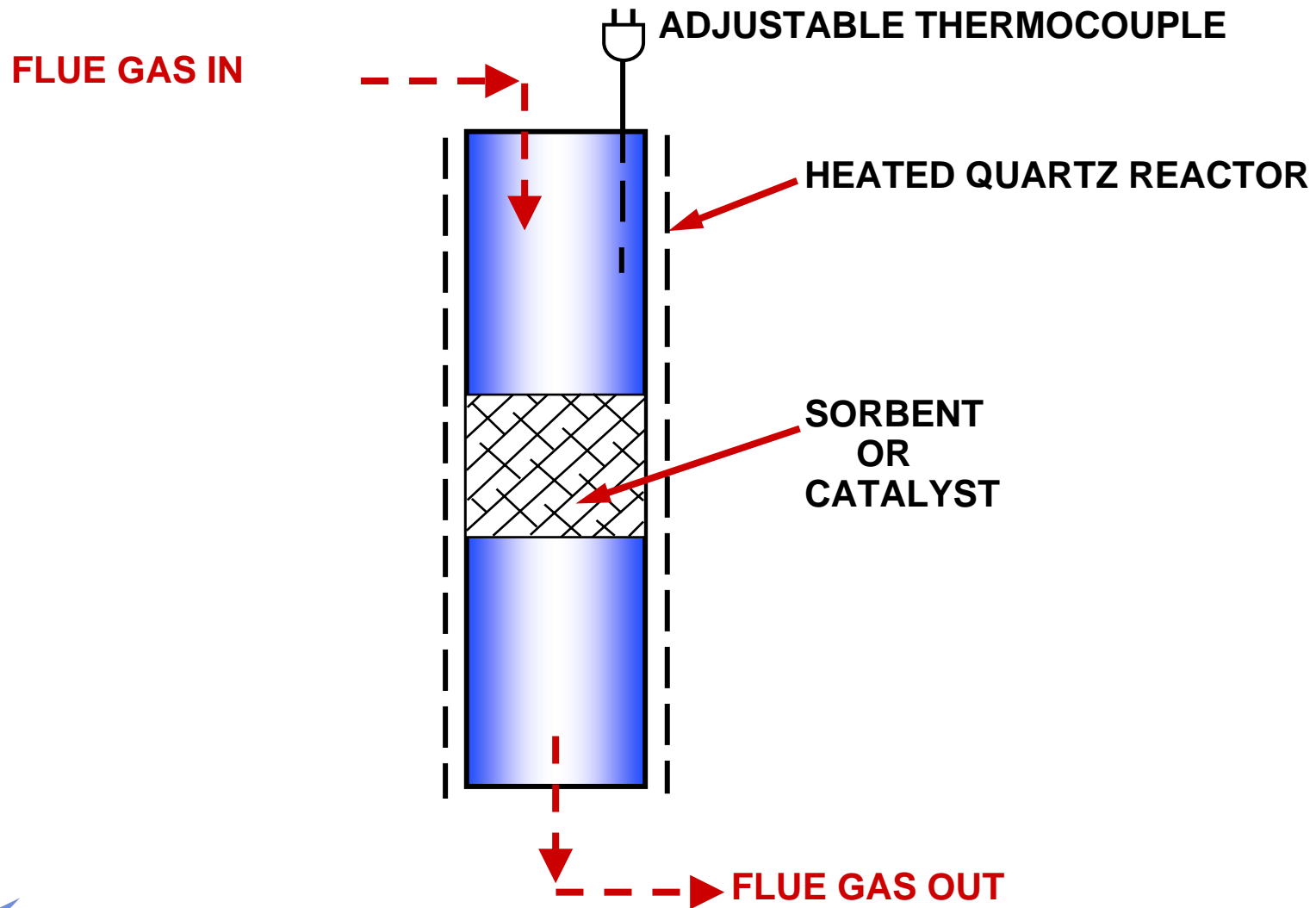
# Possible Mechanisms for SO<sub>x</sub> Effect

- **Competitive adsorption between Hg & SO<sub>x</sub>, continued**
  - **SO<sub>3</sub> adsorbs to activated carbon**
    - $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$
    - SO<sub>3</sub> can also react with surface oxygen to form H<sub>2</sub>SO<sub>4</sub>
    - **AC catalysts for H<sub>2</sub>SO<sub>4</sub> are self-poisoned by SO<sub>3</sub>**
- **Activated carbon catalyzes formation of flue gas halides**
  - $\text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2\text{Cl}_2$
  - Reaction can remove surface-bound halogens
  - Analogous reactions for NO and CO

# Typical Experimental Method

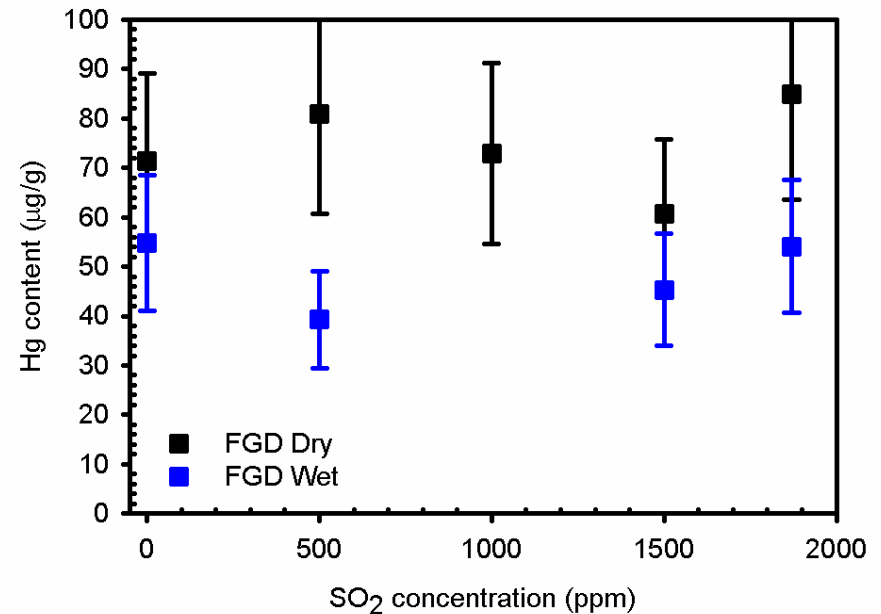
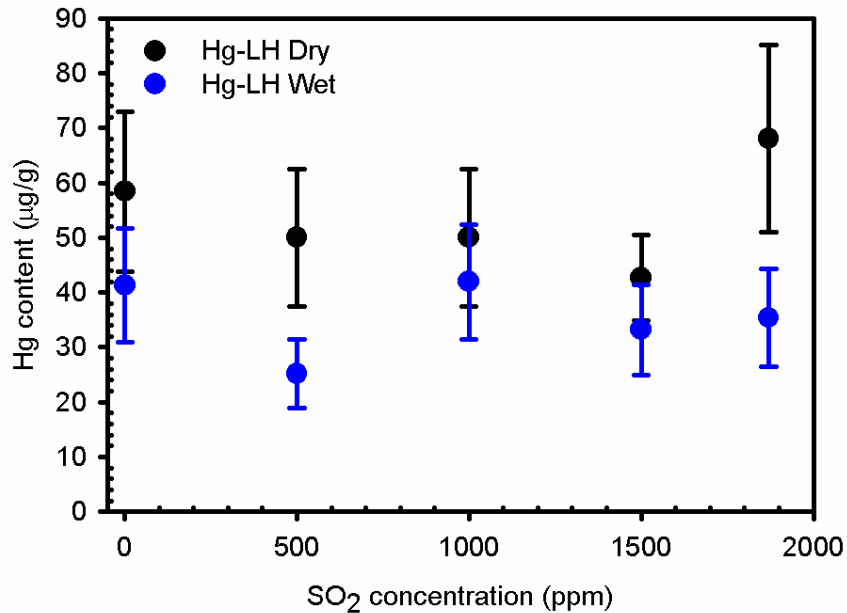
- **Test activated carbons (Darco FGD and Hg-LH) in a packed-bed reactor**
  - Realistic Hg concentration:  $9.3 \mu\text{g Nm}^{-3}$
  - Temperature:  $300^\circ \text{F}$
  - 200 mg activated carbon
- **Expose carbons to simulated flue gas (SFG)**
  - 5.3%  $\text{O}_2$ , 12.5%  $\text{CO}_2$ , 0 – 1.5%  $\text{H}_2\text{O}$ , 500 ppm NO, 50 ppm HCl
  - Vary  $\text{SO}_2$  concentration from 0 – 1870 ppm; wet and dry SFG
  - Vary  $\text{SO}_3$  concentration from 0 – 100 ppm; dry SFG only
  - 6 hour exposure time
- **Analyze exposed carbons for mercury content ( $\mu\text{g/g}$ ) and sulfur content via ICP-AES**
  - Monitor gas-phase species with mass spectrometer (MS)

# Experimental Method



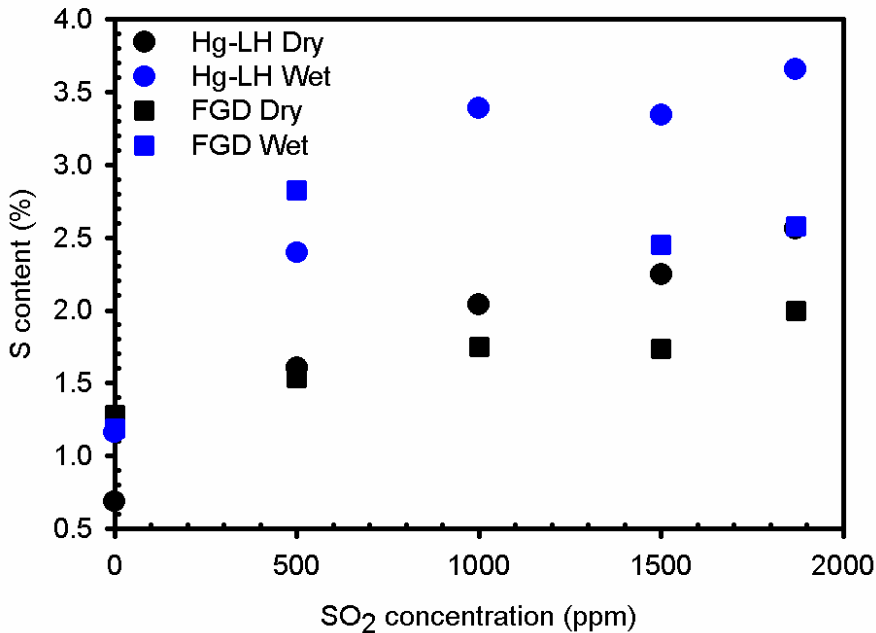


# Results: Hg Capture



***Hg capture is independent of SO<sub>2</sub> concentration***

# Results: S Content



- **Initial S content of AC**
  - 0.7 – 1.3%
- **Hg-LH captures more sulfur than FGD**
  - Hg-LH is superior for Hg capture, and SO<sub>2</sub> adsorbs to the same sites as Hg
- **More sulfur is captured when water is present in the SFG**
- **XPS data show that sulfur exists as sulfate on the AC surface**

# Results: Hg Competition with SO<sub>x</sub>

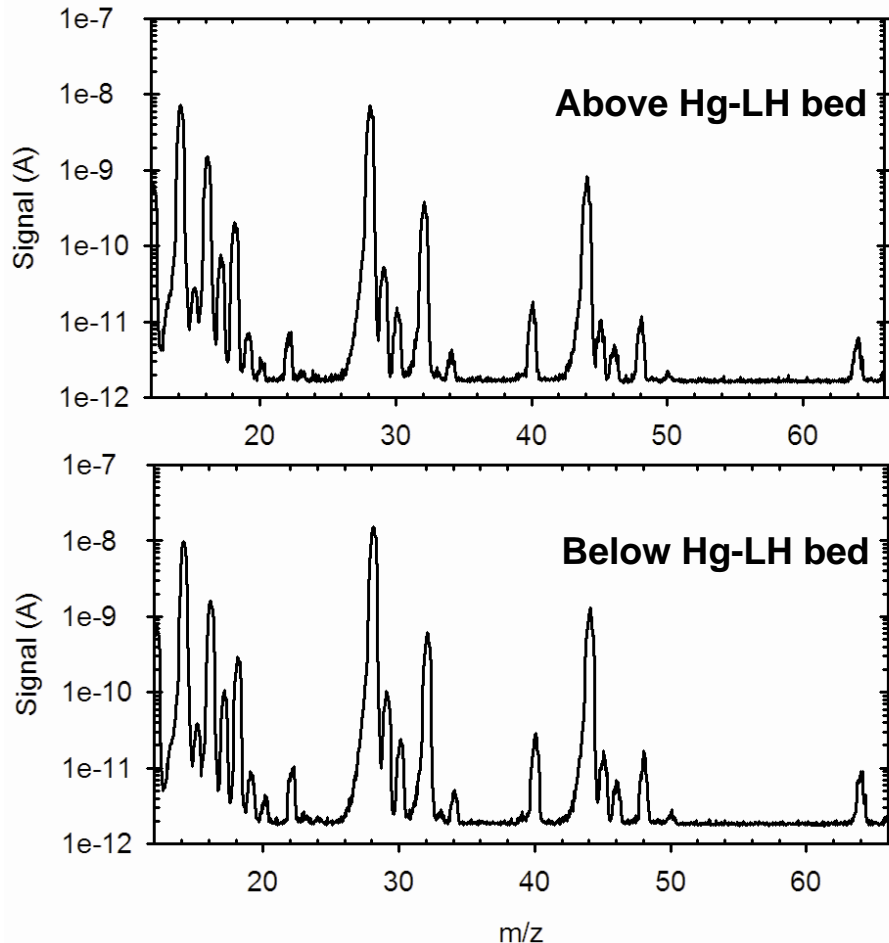
- **SO<sub>3</sub>-free experiments**

- Hg content is independent of SO<sub>2</sub> concentration (0 – 1870 ppm) in the SFG
- Sulfur exists as sulfate on the AC surface
- Water vapor (1.0 – 1.5%) reduces Hg capture by ~30%
- Darco FGD captured more Hg than Darco Hg-LH
  - During tests of ACI, brominated carbons are typically superior to unpromoted carbons
  - May result from excellent gas-solid contact in the packed bed, but poor contact in flight

# Results: Hg Competition with SO<sub>x</sub>

- **Experiments using SO<sub>3</sub> (20 – 100 ppm)**
  - **Two routes of SO<sub>3</sub> exposure**
    - Vary concentration in the SFG from 20 – 100 ppm
    - Pre-expose AC to 50 ppm SO<sub>3</sub> for 1 hour
  - **Adding SO<sub>3</sub> gave higher S content than SO<sub>2</sub> alone**
    - 1870 ppm SO<sub>2</sub> and Hg-LH → 2.5% S (dry SFG)
    - 20 ppm SO<sub>3</sub> and Hg-LH → 3% S
  - **SO<sub>3</sub> reduced the final mercury content**
    - 20 ppm SO<sub>3</sub> reduced Hg by 80%
    - Higher concentrations of SO<sub>3</sub> lead to lower Hg content
    - Both methods of SO<sub>3</sub> exposure reduce Hg content – evidence that SO<sub>3</sub> is favored both kinetically and thermodynamically

# Method of Hg Capture Inhibition: Mass Spectrometer Scans



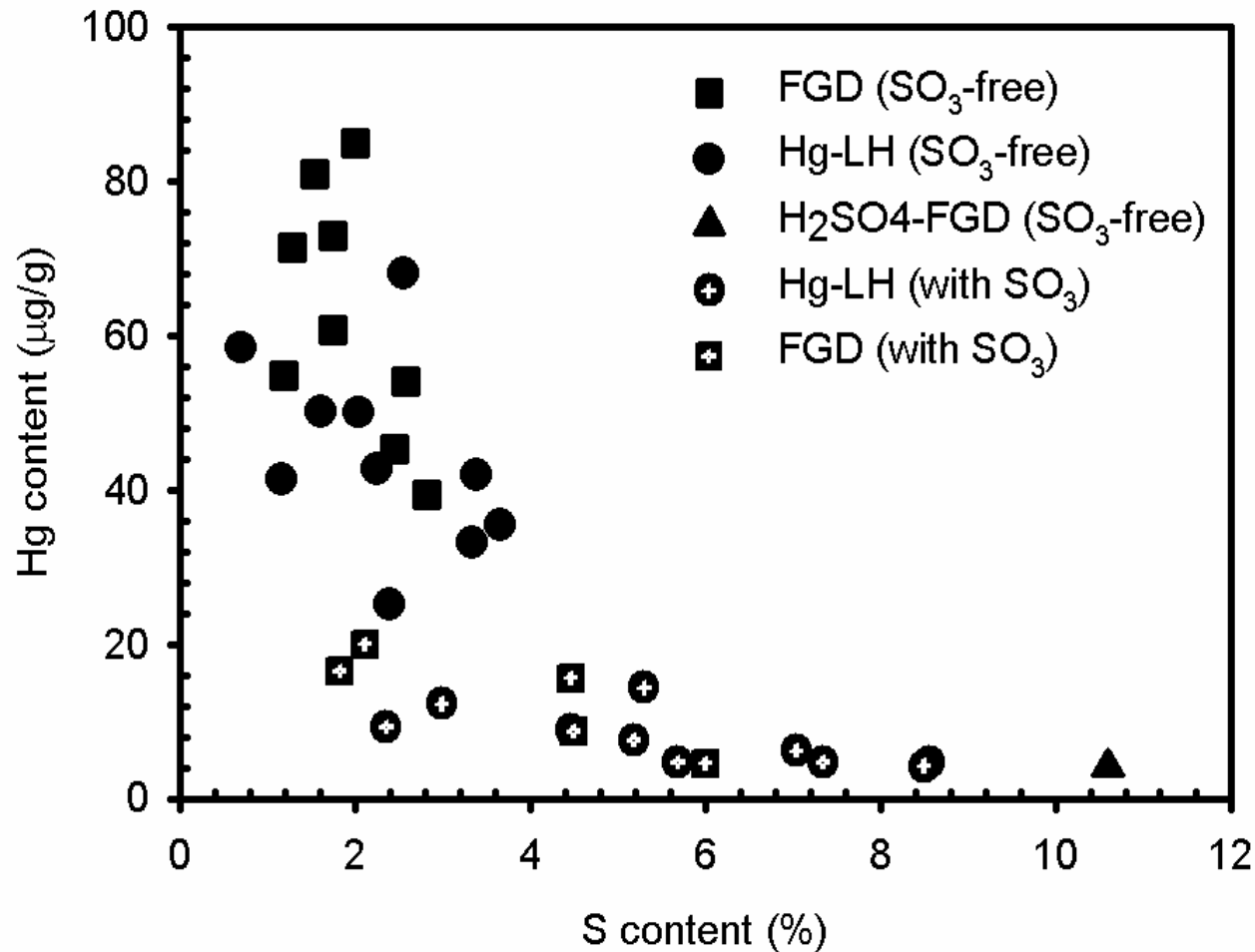
- $\text{SO}_2 = 1870$  ppm
- MS data show no evidence of flue gas halides
  - Does not rule out formation of halides
  - Easily hydrolyzed
  - Perhaps below detection limit?
- Concentrations above and below bed are constant

***Mercury capture inhibition because of flue gas halide formation is unlikely***

# Method of Hg Capture Inhibition: Competitive Adsorption

- **Does the data show a contradiction?**
  - SO<sub>2</sub> in SFG has no effect on Hg capture
  - SO<sub>3</sub> in SFG greatly reduces Hg content
  - Both SO<sub>2</sub> and SO<sub>3</sub> increased the sulfur content of the AC
- **If Hg and SO<sub>x</sub> compete for the same sites on the AC surface, then the **sulfur content** is the important variable**

# Method of Hg Capture Inhibition: Competitive Adsorption



# Method of Hg Capture Inhibition: Competitive Adsorption

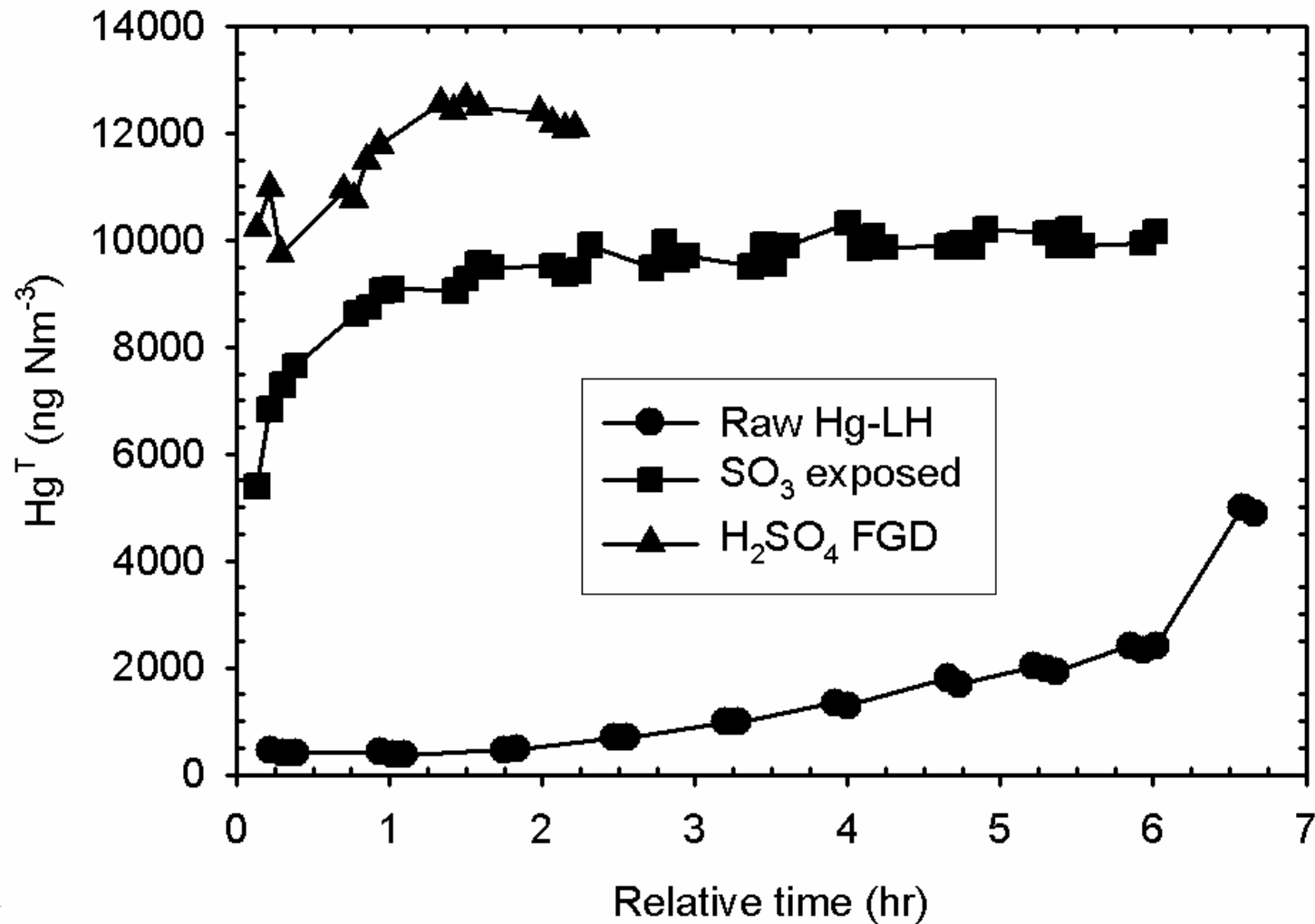
- **Hg content decreases as S content increases**
  - Almost no Hg capture for S content > 6%
    - H<sub>2</sub>SO<sub>4</sub>-FGD (10.6% S) captured almost no mercury
  - Strong evidence for competitive adsorption
- **SO<sub>3</sub> appears to have a stronger effect than SO<sub>2</sub> for a given S content**
  - May result from physically-bound SO<sub>2</sub> that does not inhibit Hg capture



# On-Line Mercury Breakthrough Experiments

- **PS Analytical Sir Galahad CEM used to verify that sulfur inhibits initial mercury capture**
  - Prior experiments assume capacity reflects in-flight capture
- **SFG composition: 10 - 12  $\mu\text{g Hg/Nm}^3$ , 5.3%  $\text{O}_2$ , 12.5%  $\text{CO}_2$ , 500 ppm  $\text{SO}_2$ , 50 ppm  $\text{HCl}$ , balance  $\text{N}_2$** 
  - $\text{NO}_{(\text{gas})}$  omitted because it interfered with Hg detection
- **Three carbons tested**
  - Raw Darco Hg-LH (0.7% S)
  - Hg-LH exposed to 100 ppm  $\text{SO}_3$  for 2 hours (8.4% S)
  - $\text{H}_2\text{SO}_4$ -FGD (10.6% S)

# Mercury Breakthrough Data



# Results: Mercury Breakthrough

- **Mercury capacity and time to 100% breakthrough decreased as S increased**
  - Raw Hg-LH
    - Captured  $125 \mu\text{g g}^{-1}$
    - 10% breakthrough after 3 hrs
  - $\text{SO}_3$ -exposed Hg-LH
    - Captured  $8.4 \mu\text{g g}^{-1}$
    - 55% initial breakthrough
    - 100% breakthrough after 3.5 hrs
  - $\text{H}_2\text{SO}_4$ -FGD
    - Captured  $<0.5 \mu\text{g g}^{-1}$
    - $>80\%$  initial breakthrough
    - 100% breakthrough after 1 hr

# Results: Mercury Oxidation

- **All samples oxidized  $\text{Hg}^0$  to  $\text{Hg}^{2+}$**
- **At 100% breakthrough**
  - $\text{SO}_3$ -exposed Hg-LH oxidized 60% of inlet  $\text{Hg}^0$
  - $\text{H}_2\text{SO}_4$ -FGD oxidized 30% of inlet  $\text{Hg}^0$
- **Previous research indicated that Hg oxidation requires surface-bound Hg**
  - Mercury oxidation at 100% breakthrough may indicate multiple active sites for mercury interaction

# Multiple Hg Sites

- **SO<sub>2</sub> forms bonds to carbon surface with energy of adsorption <50 kJ mol<sup>-1</sup> and >80 kJ mol<sup>-1</sup>**
- **SO<sub>2</sub> and Hg compete for binding sites**
- **By analogy, we can generalize**
  - Sites with high binding energy for capturing Hg
  - Catalytic sites with low binding energy for Hg
- **Mercury-surface binding energy dependent on specific surface functional groups**
  - Binding energies decrease in series for  
lactone > carbonyl > phenol > carboxyl

# Multiple Hg Sites: Hypothesis

- **High binding energy sites are occupied first**
  - Mercury is strongly bound
  - Responsible for mercury capacity
- **Catalytic sites (low binding energy)**
  - Allow mercury to easily adsorb and desorb
  - Mercury desorbs as  $\text{Hg}^{2+}$
- **$\text{SO}_3$  follows a similar path**
  - Binds to high binding energy sites first
    - Reduces Hg capacity
  - Binds to catalytic sites as high energy sites become filled
    - Less oxidation across  $\text{H}_2\text{SO}_4$ -FGD bed
  - High enough S(VI) loadings could render activated carbon useless as either a sorbent or a catalyst

# Conclusions

- **Hg capture is inhibited by competitive adsorption with  $\text{SO}_x$  species**
- **Hg capture is independent of  $\text{SO}_2$  concentration (0 – 1870 ppm) and is reduced by  $\text{SO}_3$  (20 – 100 ppm)**
- **S content is a more important variable than the gas-phase  $\text{SO}_x$  concentration**
  - Hg content decreases as S content increases
  - Sulfur on the activated carbon exists primarily as sulfate, which competes with Hg for binding sites
- **There is no evidence of persistent flue gas halide formation**

# Conclusions

- **Increasing S content reduces mercury content after 6 hrs exposure and mercury capture efficiency on shorter timescale**
- **There is evidence for multiple mercury binding sites on the carbon surface**
  - High energy sites capture mercury
  - Catalytic low energy sites



# Implications for Future Work

- **Common chemical alterations (i.e., bromination) may not overcome  $\text{SO}_x$  impact on Hg capture**
  - Bromination makes Hg-accepting sites more reactive, and therefore makes the AC more reactive towards  $\text{SO}_x$

## Potential Solutions

- **Co-injection of basic sorbents**
- **Sulfur removal upstream of ACI**
- **ACI upstream of  $\text{SO}_3$  flue gas conditioning**
- **Alternative flue gas conditioning agents**
- **Reformulated SCR Catalysts**
- **Challenge: Maintain Hg capture efficiency similar to low-S flue gas**

# Interesting Notes

## S<sup>6+</sup> Inhibits Hg Flue Gas Capture by Carbons

- **S<sup>6+</sup> : SO<sub>3(gas)</sub>, Sulfate<sub>(surface)</sub>, and H<sub>2</sub>SO<sub>4(surface)</sub>**  
**However --**
- **Sulfuric-Acid Carbons Remove Hg from Hydrocarbon Liquids and Nitrogen Gas Streams**
- **Sulfuric Acid Scrubbers for Hg Capture from Smelter Gases – Mercuric Sulfate Precipitates Out**
- **Mercury Sulfates Previously Proposed as End Product on Activated Carbons**
- **Surface Oxygen Tied up by SO<sub>3</sub>, Reduce Capacity**



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